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ON THE IMPURITIES IN FLUORITES

(Studies on the Fluorites from Japan, II)

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1. Introduction

I have studied fluorites from 20 different localities by chemical and spectrographic analyses to ascertain the crystallization of fluorites¹⁾. But, afterward, I studied types of presence and properties of impurities in fluorites and those influences to crystals, by spectrographic analyses and microscopic observations.

I wish to express my sincere thanks to Prof. Z. HARADA for his kind guidances throughout this work, and also thank to I. KAYAMA for his helps in spectrographic analyses.

2. Microscopic observations

As we observe the fluorite crystals closely, we can see the impurities, bubbles etc. inside crystals. So I made thin crystal plates, parallel to (111), cleavage plane, ca 1-3 mm. in thickness; and then observed them under binocular microscope. There are many ovals or irregular shaped cavities, parallel to [111] direction. (Fig. 1, 2 and 3). And they contain liquids, gases, or mafic minerals, and sometimes empties. Also fragment of rocks, specks of kaolin etc. are contained in those cavities near surface; and those cavities can not see quite

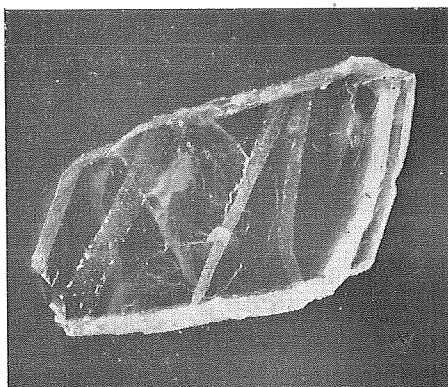


Fig. 1. Observation of (111), cleavage plane, ca 1-3 mm. in thickness. $\times 10$
Green fluorite from Fuso Mine, Korea.

1) T. SAITO: Jour. Fac. Sci. Hokkaido Univ., Ser. IV, No. 3. 1950. 307-314.

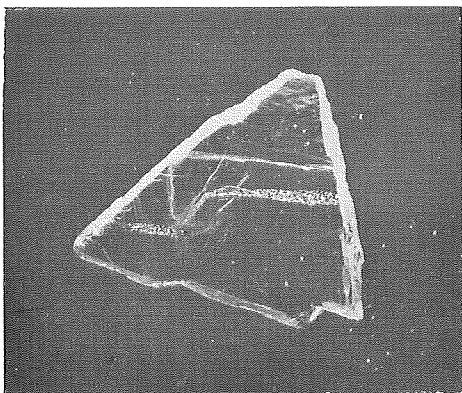


Fig. 2. Observation of (111), cleavage plane, ca 1-3 mm. in thickness.

× 10.

Colourless fluorite from Obira, Oita Pref, Japan.

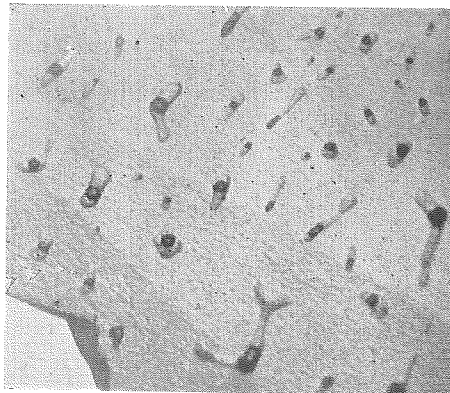


Fig. 3. Many ovals or irregular shaped cavities, parallel to (111), ca 1-3 mm. in thickness. × 56.

Blue fluorite from Hayakawa Mine, Hokkaido, Japan.

interior of crystals. Moreover each cavities are isolated, not connected with each other.

From above facts, we shall conclude that formation of those cavities are connected to crystal growth, not in secondary origin.

And in thin section, quartz and sericite etc. are formed in cracks of crystals. But they are considered to be formed in crystals secondarily, and they are found in abundance in the massive crystals particularly.

3. Microchemical test

From above observations, I selected pieces of crystal specimens, containing many cavities, and made microchemical tests²⁾ on those specimens. Following results were obtained as shown in Table I. From these results, it is obvious that Fe, Mn and Ni etc. are contained in the crystals from hydrothermal origins with some exceptions and Co, Cu and Pb etc. are found in the crystals from contact metamorphic origins. These results are almost similar to those of spectrographic analyses in the previous report,³⁾ and we can conjecture the types of presence of those minor components.

Moreover following expectation will be made that those minor compo-

2) M. N. SHORT: Microscopic Determination of the Ore Minerals. Washington. (1940). 185-292.

3) T. SAITO: loc. cit.

nents are not existed as minerals, but are contained as liquids or gases in the cavities on cleavage plane or in cracks, almost parallel to (111). Also those presumptions are ascertained by following acid-treatment test.

TABLE I. Microchemical test.

Locality	Occurrence	Fe	Mn	Ni	Co, Cu	Pb	Zn	As
Ishigure, Mie Pref.	fluorite vein	+	+	—	—	—	—	—
Kano Mine, Fukushima Pref.	"	+	(+)	(+)	(+)	—	—	—
Rhyka Mine, Manchuria.	"	+	(+)	(+)	—	—	—	—
Fuso Mine, Korea.	"	+	—	(+)	(+)	—	—	—
Obira, Oita Pref.	contact deposit	+	—	—	+	+	—	—
"	"	(+)	—	—	+	—	—	—

+ existence. (+) trace. — non existence.

4. Acid-treatment test

Crystalline parts of fluorites were ground into powder (ca 250 mesh) and it was heated with 1-N hydrochloric acid, for six hours on a water bath. And following changes of minor elements in the treatments by 1-N hydrochloric acid were obtained as shown in Table II.

From this table, it is obvious that there are two types of minor

TABLE II. Changes of minor elements in the treatment by 1-N hydrochloric acid.

Locality	Element treatment	Mn	Ti	Mg	V	Ni	Co	Mo	Cu	Be	Ce	Pb	Zr	Rh	Ru
Ishigure, Mie Pref.	before	+	+	+	+	...	...	...	...	...	...	...	...	...	...
	after	—	(+)	—	+	...	...	...	...	...	...	...	...	...	...
Kano Mine, Fukushima Pref.	before	+	(+)	+	+	+	+	...	...	...	...	...	...	...	...
	after	(+)	(+)	—	+	—	—	...	...	...	...	...	...	...	...
Rhyka Mine, Manchuria.	before	+	+	+	+	+	...	...	...	+	?	...	...	...	...
	after	—	(+)	—	+	—	...	...	...	—	—	...	...	...	...
Fuso Mine, Korea.	before	+	+	...	+	+	+	...	+	...	...	+	+	(+)	?
	after	—	(+)	...	+	—	—	...	—	...	...	—	—	—	—
Obira, Oita Pref.	before	(+)	+	...	+	...	...	...	...	...	...	...	...	...	...
	after	—	(+)	...	+	...	...	...	...	...	...	...	...	...	...
"	before	...	+	...	+	...	+	+	+	...	+	...	...	...	...
	after	...	(+)	...	+	...	—	—	—	...	—	...	...	...	...

+ existence. (+) trace. — non existence.

elements, soluble one (Mn, Mg, Ni and Fe etc.) and insoluble one (Ti and V) by dilute hydrochloric acid. As we know that those elements have not selective solubility for hydrochloric acid⁴⁾, so we can conjecture types of presence of such soluble elements, these facts support the above thoughts. Namely, as we think in connection with the above observations or tests, it shall be suggested that elements being solved by acid have no relation to CaF_2 lattice, and are contained in fluorite crystals by adsorption only or in cavities. But on Ti and V exact relations are not obvious.

5. Difference of minor elements on crystal planes

Specimens, parallel to (111), (110) and (100), were picked out respectively. And distribution of minor elements were studied on each specimens by spectrographic analyses. Following results were obtained as shown in Table III. From this table, it is obvious that (111) plane are more concentrated by minor elements than another two planes, (110) and (100). As crystal faces are three dimensional, these results may be not always mean contained elements on certain face. But it is almost obvious that Ni, Fe, Mg, Mn and Co etc. are concentrated in (111), and Ti and V have not selective concentration on definite crystal face comparatively.

TABLE III. Difference of minor elements on crystal planes, (110), (111) and (100).

Locality	Element Plane	Mn	Ti	Mg	V	Ni	Fe	Co	Ce	Be	Rh
Hayakawa Mine, Hokkaido.	(110)	A	M	T	M	A	T			A	
	(111)	VS	VS	VS	M	VS	VS			M	
	(100)	T	M	T	M	T	T			A	
Rhyka Mine, Manchuria.	(110)	T	M	T	M	T	T	A	A		A
	(111)	M	VS	VS	M	VS	VS	T	?		?
	(100)	M	M	T	T	T	T	A	A		A

A: not detected. T: trace. M: medium. VS: very strong.

4) A. SEIDELL: Solubilities of Inorganic and Organic Compounds. Vol. 1-2. New York. (1919).

6. Consideration

Hitherto, fluorites have been thought to be pure CaF_2 . But I knew that they contained always impurities by minute studies. And those impurities may be contained accidentally; but it shall be considered that contained impurities in fluorites exert influence upon crystal growth of fluorites, associating with the effect of pressure and temperature. So on the effects of the adsorbed foreign substances upon crystal growth or crystal habit, many studies have been reported already⁵⁾; particularly NaCl ⁶⁾, KClO_3 ⁷⁾, NaClO_3 ⁸⁾, K_2SO_4 ⁹⁾ and KMnO_4 ¹⁰⁾ etc. in detail.

Moreover, C. FRONDEL¹¹⁾ says "Slow growth, in general, enhances the size and perfection of crystals, as was brought out in this connection by ZWICKY, and the effect of a adsorbed foreign substances may possibly be by slowing up growth. This view is supported by the frequent occurrence of habit modification in such cases, and is not inconsistent with the fact that under other circumstances addition agents may cause the formation of fine grained aggregates or of skeletal growths, in place of normal crystals, as a result of an extreme hindering of growth."

Also, H. HABERLANDT¹²⁾ studies the relations between impurities and a cause of colouring of fluorites, and he says "Abschliessend kann gesagt werden, dass die Farbverteilung beim Fluorit durch Fremdstoffe (aktive Verunreinigungen, sulfidische Einlagerungen, seltene Erden) bedingt ist, welche entsprechend dem Kristallbau während des Wachstums gesetzmässig eingelagert werden."

From above microscopic observations, acid-treatment test and difference of minor elements in crystal faces on fluorites, it shall be considered that those elements are not contained in CaF_2 lattice (Ti and V are not obvious), but are adsorbed only, and they are not always formed as minerals but mainly type of solution or gas in cleavage along

5) It is collected in "Handbuch der Physik. II, Berlin. (1933). 816. by H. GEIGER u. K. SCHEEL."

6) T. YAMAMOTO : Sci. Pap. I.P.C.R. 10 (1932) ~ 15 (1936).

7) H. E. BUCKLEY : Z. Krist. 82 (1932). 11, 37.

8) " : Z. Krist. 75 (1920). 15.

9) " : Z. Krist. 88 (1934). 122, 248.

10) " : Z. Krist. 78 (1931). 412.

11) C. FRONDEL : Am. Min. 20 (1935). 471.

12) H. HABERLANDT u. A. SCHIENER : Z. Krist. 90, (1935), 193.

(111) plane. Moreover it shall be suggested that these impurities are not adsorbed accidentally nor secondarily, but they will be taken rationally at the time of crystal growth and they will play some important roles of affects to formation of crystal face, associating with pressure or temperature.

7. Summary

Following results are obtained from the above researches.

1. It is considered that impurities in fluorites are fixed in cavities on cleavage or in cracks along (111) plane as liquids or gases mainly, and they are not fixed CaF_2 lattice generally.
2. Those cavities are not in secondary origin, but are formed during crystal grows.
3. Certain intimate relations exist between components being contained in cavities and occurrence of fluorites. For example, cavities in fluorites from hydrothermal ore deposits are contained Fe, Ni and Mn etc.
4. Impurities being contained on each plane ((111), (100) and (110)) are not equal in concentration, namely impurities concentrate on (111) plane more than on another planes.
5. It shall be suggested that the difference of contained impurities and minor components have certain relations to crystal growth, and these differences will be some important factors on growing in fluorites.